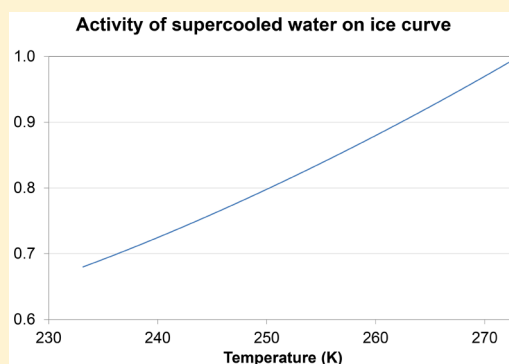


# Activity of Supercooled Water on the Ice Curve and Other Thermodynamic Properties of Liquid Water up to the Boiling Point at Standard Pressure

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**ABSTRACT:** A simple model for thermodynamic properties of water from subzero temperatures up to 373 K was derived at ambient pressure. The heat capacity of supercooled water was assessed as lambda transition. The obtained properties for supercooled water such as heat capacity, vapor pressure, density and thermal expansion are in excellent agreement with literature data. Activity of water on ice curve, independent of used electrolyte and Debye–Hückel constant applied in modeling, is also calculated. Thus, the ice curve activity of supercooled water can be used as a universal basis for thermodynamic modeling of aqueous solutions, precipitating hydrated and anhydrous solids. A simple model for heat capacity, density and thermal expansion of ice are also derived from 170 K up to melting point.



## INTRODUCTION

The peculiar thermodynamic properties of supercooled water and its practical importance for modeling aqueous solution at subzero temperatures (e.g., ref<sup>1</sup>) have been gaining more and more attention. The thermodynamic properties of liquid water are well-known over 273.15 K at standard pressure but are still ambiguous below 273.15 K mainly due to anomalies in its thermophysical properties caused by hydrogen bonds.<sup>2–6</sup>

The thermodynamic properties of supercooled liquid water in equilibrium with ice Ih, that is, the ice curve, are generally obtained by the assessment of experimental ice curve data for one or more electrolytes. However, the activity of water on the ice curve is independent of the studied electrolyte system and it depends only on the thermodynamic properties of ice and pure metastable supercooled water.<sup>7,8</sup> Similar results are obtained also for homogeneous<sup>8</sup> and heterogeneous ice nucleation.<sup>9</sup>

Freezing point depression is used among other Gibbs energy related experimental data when fitting activity coefficient parameters. Usually in evaluation of the activity of water at subzero temperatures, the heat capacity difference between supercooled liquid water and solid ice ( $\Delta C_p$ ) is assumed either insignificant, that is zero, or independent of temperature. However, the heat capacity of supercooled water starts to increase rapidly below  $-10\text{ }^{\circ}\text{C}$  while the heat capacity of ice decreases steadily, so the assumption of constant heat capacity difference below  $-10\text{ }^{\circ}\text{C}$  is not usable in accurate thermodynamic modeling. Moreover, the calculated activity of water in subzero aqueous solutions will also depend on the equation used for the Debye–Hückel constant. Both items reflect also to the estimated vapor pressure of water solution at subzero temperatures, which is important in meteorological and climate models.

The purpose of this study is to generate a practical thermodynamic expression for the supercooled liquid water for modeling purposes of aqueous electrolyte systems in 1 atm total pressure. The aim is to simplify the universal approach in the T–P domain (e.g., ref 10) for tools and thermodynamic descriptions available in most software used in various engineering approaches of thermodynamic modeling and aqueous simulation.

## THEORY

In aqueous solution the chemical potential of the solvent, that is water, is defined as

$$\mu_w(T, p) = \mu_w^{\circ}(T, p) + RT \ln(a_w^s) \quad (1)$$

where the standard state for a solution is pure liquid water at temperature and pressure of the solution and  $a_w$  is the activity of liquid water. Superscript s indicates a solution,  $R$  is the gas constant, and  $T$  is temperature in Kelvin.

The chemical potential of pure liquid water at any temperature and pressure is

$$\mu_w^*(T, p) = \mu_w^{\circ}(T) + RT \ln(a_w^*) \quad (2)$$

where the standard state of pure liquid is a pure liquid at standard pressure,  $p^{\circ}$ . The star refers to pure liquid and  $a_w$  is the activity of pure liquid water. Standard pressure used in this article is 101.325 kPa. As far as condensed phases are considered the thermodynamic properties are practically equal at 101.325 kPa (1 atm) and 100 kPa (1 bar) pressure.

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Activity is always related to chosen standard state so we obtain for activity of pure liquid water:

$$RT \ln(a_w^*) = \int_{p^o}^p v_w^* dp \quad (3)$$

where  $v_w$  is the molar volume of liquid water.

So, for the chemical potential of liquid water in solution we obtain

$$\begin{aligned} \mu_w(T, p) &= \mu_w^o(T, P) + RT \ln(a_w^s) \\ &= \left[ \mu_w^o(T) + \int_{p^o}^p v_w^* dp \right] + RT \ln(a_w^s) \end{aligned} \quad (4)$$

Similarly for the chemical potential of ice:

$$\mu_{ice}^*(T, p) = \mu_{ice}^o(T) + \int_{p^o}^p v_{ice}^* dp \quad (5)$$

**Equilibrium between Liquid Water in a Solution and Ice.** When supercooled liquid water is in equilibrium with pure solid ice the chemical potentials of water are equal:

$$\begin{aligned} \mu_w(T, p) &= \mu_{ice}^*(T, p) \Leftrightarrow \mu_{ice}^o(T) + \int_{p^o}^p v_{ice}^* dp \\ &= \mu_w^o(T) + \int_{p^o}^p v_w^* dp + RT \ln(a_w^s) \end{aligned} \quad (6)$$

Thus, solving activity for supercooled water in a solution in equilibrium with ice, yields

$$\begin{aligned} RT \ln(a_w^s) &= \mu_{ice}^o(kT) + \int_{p^o}^p v_{ice}^* dp - \mu_w^o(T) - \int_{p^o}^p v_w^* dp \\ &= -\Delta G^o - \int_{p^o}^p \Delta v dp \end{aligned} \quad (7)$$

where

$$\Delta G^o = \mu_w^o(T) - \mu_{ice}^o(T) \quad (8)$$

$$\Delta v^* = v_w^* - v_{ice}^* \quad (9)$$

At standard pressure  $p^o$  the integral term is zero so

$$RT \ln(a_w^s) = -\Delta G^o = RT \ln K \Rightarrow a_w^s = K \quad (10)$$

**Table 1. Heat Capacity Data for Liquid Water Used in the Assessment**

authors	temp range (K)	no. expts included	excluded	weight
NIST <sup>22</sup>	273.15–373.756	100	$T > 374$ K	1
Wagner and Pruss <sup>23</sup>	274–372	50	$T \geq 374$ K	1
Speedy <sup>15</sup>	236.05–257.05	8	236.05 K	0.5
Angel et al., <sup>24a</sup>	236–270	9	236 K	0.5
Angel et al. <sup>19,20,24b</sup>	236–290	0	all values	0
Archer and Carter <sup>12</sup>	235–285	0	all values	0

<sup>a</sup>Suggested values in their Table 1. <sup>b</sup>Measured values in their Table 1 (ref 24).

**Table 2. Fitted Parameters for Heat Capacity of Water  $C_p$**

range	temp range (K)	$K_A$	$A_i$	$B_i$ (K <sup>-1</sup> )	$D_i$ (K <sup>2</sup> )
1	237–262.15	5.4943	−255.07	1.07493	
2	262.15–298.15		134.4	−0.385856	$6.29422 \times 10^{-4}$
3	298.15–373.15		89.8098	−0.09426775	$1.53047 \times 10^{-4}$

**Table 3. Quality of the Fit for Heat Capacity of Water  $C_p$**

authors	no. expts included	RMSE J/Kmol	AARD %
NIST <sup>22</sup>	100	0.011	0.008
Wagner and Pruss <sup>23</sup>	50	0.011	0.008
Speedy <sup>15</sup>	8	0.53	0.50
Angel et al. <sup>24</sup>	9	0.57	0.54

Thus the activity of supercooled water in equilibrium with ice at standard pressure can be calculated if the Gibbs energy change or the equilibrium constant for reaction  $H_2O(\text{ice}) = H_2O(\text{l})$  is known. Moreover, it is independent of the electrolytes in the solution.

The Gibbs energy change can be calculated from  $\Delta H_{fus}^o$  and  $\Delta C_p^o$  where  $\Delta H_{fus}^o$  is enthalpy of fusion and  $\Delta C_p^o$  is the heat capacity change between liquid water and solid ice  $\Delta C_p^o = C_{p,w}^o - C_{p,ice}^o$ .

$$\Delta G^o = \Delta H^o - T \Delta S^o \quad (11)$$

where

$$\Delta H^o(T) = \Delta H^o(T_{fus}) + \int_{T_{fus}}^T \Delta C_p^o dT \quad (12)$$

and

$$\Delta S^o(T) = \frac{\Delta H^o(T_{fus})}{T_{fus}} + \int_{T_{fus}}^T \frac{\Delta C_p^o}{T} dT \quad (13)$$

Below 273.15 K at ambient pressure, the heat capacity of ice is well-known but the heat capacity of supercooled water is more problematic, due to the metastability of liquid water. The heat capacity of supercooled water is showing  $\lambda$ -transition-like behavior so we have applied the approach used in a higher temperature system, that is, equation developed by Hillert and Jarl<sup>11</sup>

$$C_{p,w}^o = 2K_A R \left( \tau^{-5} + \frac{\tau^{-15}}{3} + \frac{\tau^{-25}}{5} \right) \quad (14)$$

where  $\tau = 1 - T/T_c$  and  $T_c$  is the critical temperature and  $K_A$  is a parameter specific to the system.

**Pressure Ratio between Pure Supercooled Liquid Water and Ice.** The chemical potential of pure water vapor is

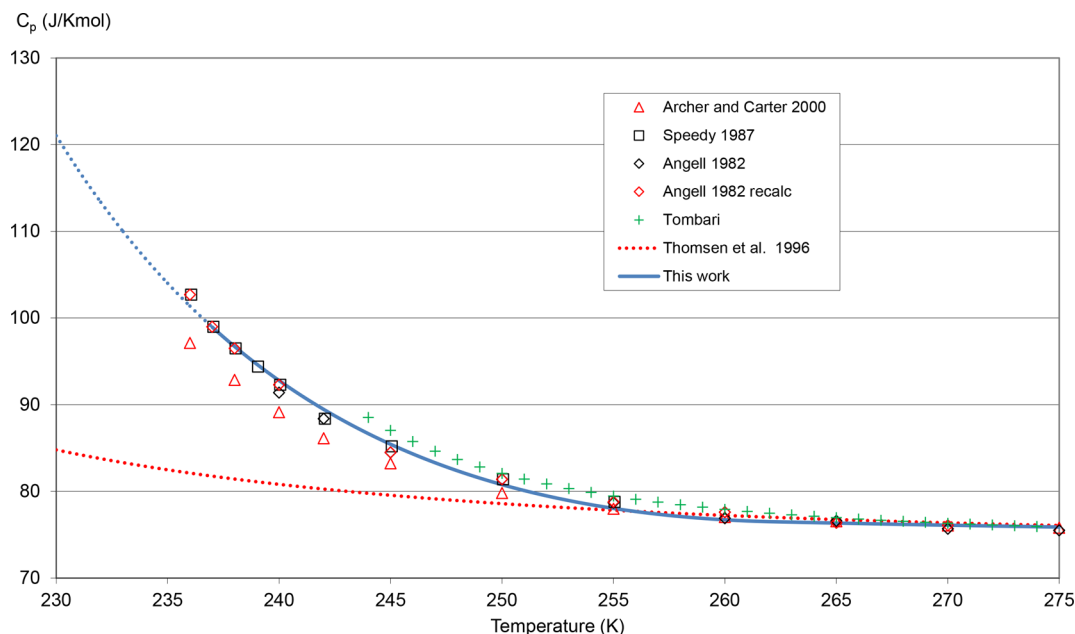
$$\mu_g^*(T, p) = \mu_g^o(T) + RT \ln(p^*/p^o) + RT \ln(\phi^*) \quad (15)$$

where the standard state for vapor is ideal gas,  $p$  is vapor pressure and  $\phi$  refers to fugacity coefficient, which can be evaluated in ambient pressure with the second virial coefficient B:

$$RT \ln(\phi^*) = B^*(T)p \quad (16)$$

In equilibrium between ice and vapor the chemical potentials are equal and we obtain from eqs 5, 15, and 16:

$$\begin{aligned} \mu_{ice}^o(T) + \int_{p^o}^{p_{ice}^*} v_{ice}^* dp \\ = \mu_g^o(T) + RT \ln(p_{ice}^*/p^o) + B^*(T)p_{ice}^* \end{aligned} \quad (17)$$



**Figure 1.** Assessed heat capacity  $C_p$  of supercooled water (line) as a function of temperature compared with experimental data<sup>12,15,24,25</sup> (dots) at subzero temperatures. Dashed line presents extrapolated values. Equation used in freezing point modeling by Thomsen et al.<sup>26</sup> is also shown in the graph.

Similarly for pure water and vapor from eqs 2, 3, 15, and 16

$$\begin{aligned} \mu_w^o(T) + \int_{p^o}^{p_w^*} v_w^* dp \\ = \mu_g^o(T) + RT \ln(p_w^*/p^o) + B^*(T)p_w^* \end{aligned} \quad (18)$$

Combining eqs 17 and 18 yields

$$\begin{aligned} \mu_w^o(T) - \mu_{ice}^o(T) + \int_{p^o}^{p_w^*} v_w^* dp - \int_{p^o}^{p_{ice}^*} v_{ice}^* dp \\ = RT \ln(p_w^*/p_{ice}^*) + B^*(T)(p_w^* - p_{ice}^*) \end{aligned} \quad (19)$$

Up to moderate pressure, molar volumes of condensed phases are insensitive to pressure so

$$\begin{aligned} \mu_w^o(T) - \mu_{ice}^o(T) + v_w^*p_w^* - v_{ice}^*p_{ice}^* - p^o(v_w^* - v_{ice}^*) \\ = RT \ln(p_w^*/p_{ice}^*) + B^*(T)(p_w^* - p_{ice}^*) \end{aligned} \quad (20)$$

Defining  $\Delta p = (p_w - p_{ice})$  yields

$$\begin{aligned} \mu_w^o(T) - \mu_{ice}^o(T) + (p_{ice}^* - p^o)\Delta v^* + v_{ice}^*\Delta p^* + \Delta v^*\Delta p^* \\ = RT \ln(p_w^*/p_{ice}^*) + B^*(T)\Delta p^* \end{aligned} \quad (21)$$

and furthermore

$$\begin{aligned} \frac{\Delta G^o}{RT} + (p_{ice}^* - p^o)\frac{\Delta v^*}{RT} + (v_{ice}^* - B^*(T))\frac{\Delta p^*}{RT} \\ + \frac{\Delta v^*\Delta p^*}{RT} = \ln(p_w^*/p_{ice}^*) \end{aligned} \quad (22)$$

Solving  $p_w/p_{ice}$  ratio yields

$$(p_w^*/p_{ice}^*) = \frac{Q_1 Q_2 Q_3}{K} \quad (23)$$

where

$$\begin{aligned} Q_1 &= \exp\left((p_{ice}^* - p^o)\frac{\Delta v^*}{RT}\right), \\ Q_2 &= \exp\left((v_{ice}^* - B^*(T))\frac{\Delta p^*}{RT}\right), \quad Q_3 = \exp\left(\frac{\Delta v^*\Delta p^*}{RT}\right) \end{aligned} \quad (24)$$

Assuming all  $Q_i$ 's equal 1 yields for the pressure of liquid water:

$$p_w^* \approx p_{ice}^*/K \quad (25)$$

Thus, the vapor pressure of pure supercooled water can be estimated from vapor pressure of pure ice, if the value of equilibrium constant is known as a function of temperature.

## COMPUTATIONAL METHODS AND RESULTS

**Heat Capacity of Liquid Water.** The heat capacity of liquid water in the temperature range  $-35$  to  $+100$  °C was modeled from experimental data using three temperature ranges. Heat capacity for supercooled water was modeled using the equation of  $\lambda$  transition by Hillert and Jarl.<sup>11</sup> During the assessment, it was found that the following equations will describe the heat capacity of liquid water when a baseline,  $A_1 + B_1T$ , to lambda transition is added.

$$\begin{aligned} C_{p,w}^o &= 2K_A R \left( \tau^{-5} + \frac{\tau^{-15}}{3} + \frac{\tau^{-25}}{5} \right) + A_1 + B_1 T \\ &\text{for } 237 \text{ K} < T \leq 262.15 \text{ K} \end{aligned} \quad (26)$$

$$\begin{aligned} C_{p,w}^o &= A_2 + B_2 T + D_2 T^2 \\ &\text{for } 262.15 \text{ K} < T \leq 298.15 \text{ K} \end{aligned} \quad (27)$$

$$\begin{aligned} C_{p,w}^o &= A_3 + B_3 T + D_3 T^2 \quad \text{for } 298.15 \text{ K} < T \leq 373.15 \text{ K} \end{aligned} \quad (28)$$

Moreover, it was found that the heat capacity data of Archer and Carter<sup>12</sup> was not at lower temperatures in agreement with the

other literature data so it was not included in the assessment. A similar conclusion was made by Holten et al.<sup>13</sup> in 2014.

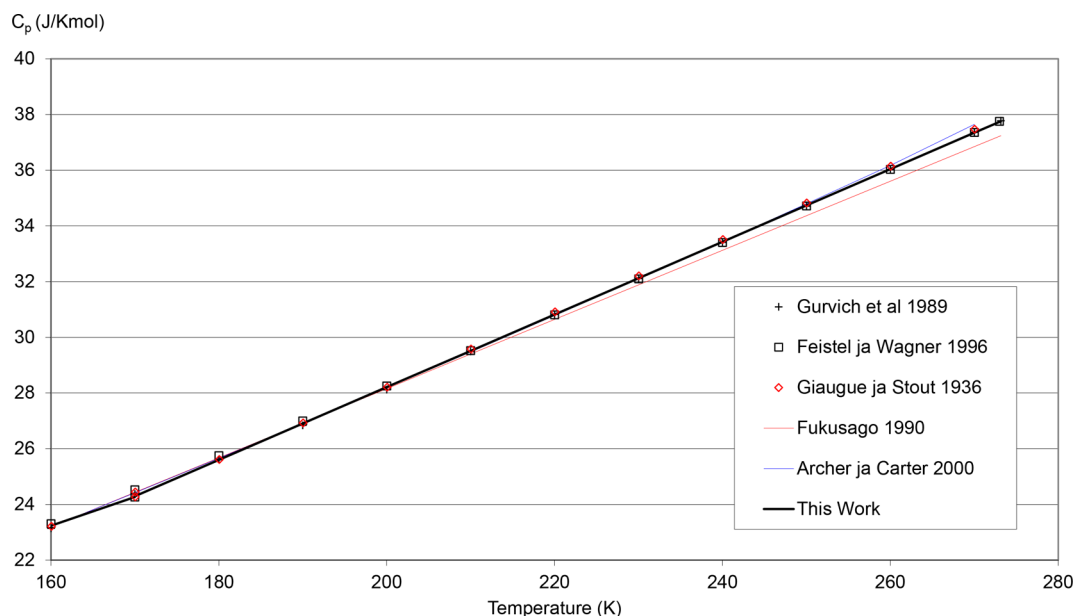
The value of critical temperature,  $T_c$ , in the literature varies from 227 K to 228 K.<sup>13–15</sup> The value of 228 K is chosen

**Table 4. Heat Capacity Data of Ice and the Obtained Correlation Coefficient  $R$**

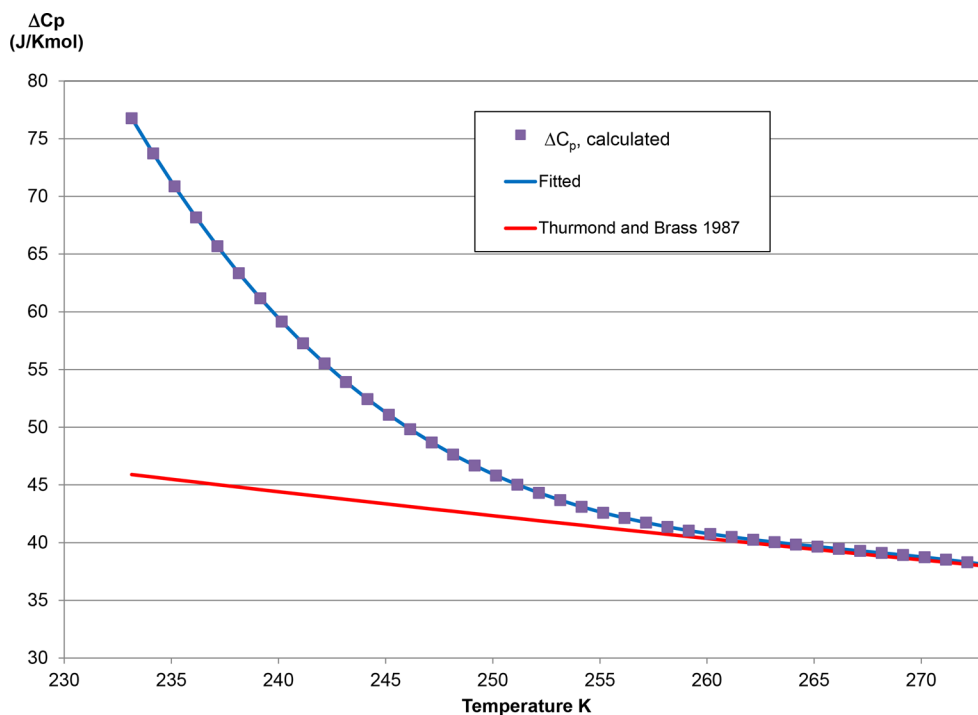
authors	temp range/K	no. expts	weight	$R$
Gurvich et al. 1989 <sup>27</sup>	170–270	12	1	0.99998
Feistel and Wagner 1996 <sup>28</sup>	170–273	12	1	0.99994
Giauque and Stout 1936 <sup>29</sup>	236.05–257.05	11	1	0.99999

to retain consistency with the HKF model.<sup>16</sup> The experimental data used are shown in Table 1 and the obtained parameters are in Table 2. The  $C_p$  data by Anisimov et al.<sup>17</sup> were not used in the assessment because of their narrow temperature interval below 273.15 K. Also, the early data of Rasmussen and MacKenzie,<sup>18</sup> Angell and Tucker,<sup>19</sup> Angell et al.,<sup>20</sup> and Oguni and Angell<sup>21</sup> were not used.

The quality of the assessments for each experimental data set is estimated by standard deviations (SD), which describes the absolute deviation, also known as root-mean-square-error (RMSE), defined as



**Figure 2.** Assessed heat capacity  $C_p$  of solid ice (black line) as a function of temperature compared with experimental data<sup>28,29</sup> (dots) and equations in the literature<sup>12,30</sup> (red and blue lines).



**Figure 3.** Assessed heat capacity change,  $\Delta C_p$ , as a function of temperature compared with the equation of Thurmond and Brass.<sup>7</sup>

**Table 5. Values for Equilibrium Constant  $K$  for the Reaction  $\text{H}_2\text{O}(\text{ice}) = \text{H}_2\text{O}(\text{l})$  at Temperatures  $-40$ – $0$  °C**

$t$ (°C)	this work	Spencer et al. <sup>32</sup>	difference
−40	0.6799	0.6805	−0.0005 <sub>7</sub>
−35	0.7120	0.7123	−0.0003
−30	0.7467	0.7469	−0.0002
−25	0.7837	0.7840	−0.0003
−20	0.8229	0.8232	−0.0003
−15	0.8641	0.8643	−0.0002
−10	0.9073	0.9074	−0.0001
−5	0.9526	0.9525	0.0001
0	1.0000	1.0002	−0.0002

**Table 6. Density Data for Liquid Water Used in the Assessment**

authors	temp. range	no. expts included	excluded	weight
Hare and Sorensen <sup>33</sup>	(−34–0) °C	35		1
Wagner and Pruss <sup>23</sup>	(273.15–373.124) K	18	$T \geq 374$ K	1

$$\text{RMSE} = \sqrt{\sum_{i=1}^N \frac{(C_i - E_i)^2}{N}} \quad (29)$$

where  $i$  goes over all included experimental points ( $N$ ), and  $C_i$  and  $E_i$  are the calculated and experimental values, respectively. Mean absolute percentage error (MAPE), also known as absolute average relative deviation (AARD %), is used to describe the relative deviation:

$$\text{AARD\%} = \frac{100}{N} \left( \sum_{i=1}^N \frac{|C_i - E_i|}{E_i} \right) \quad (30)$$

The RMSE and AARD% values of different authors used in the assessment are listed in Table 3.

A comparison with the fitted and literature values at subzero temperatures is shown in Figure 1.

**Heat Capacity of Ice.** The heat capacity of solid ice in the temperature range 170–273.15 K was fitted using the relationship  $a + b \cdot (T/\text{K})$  from the experimental data listed in Table 4.

The obtained equation for heat capacity of ice in the temperature range 170–270 K is

$$C_{p,\text{ice}}(\text{J/Kmol}) = 2.1128 + 0.130484 \cdot (T/\text{K}) \quad (31)$$

and it is compared with experimental data and the other available  $C_p$  equations in Figure 2.

**Heat Capacity Change.** The heat capacity change  $\Delta C_p^\circ$  can now be evaluated and assessed in the temperature range (237–273.15) K as

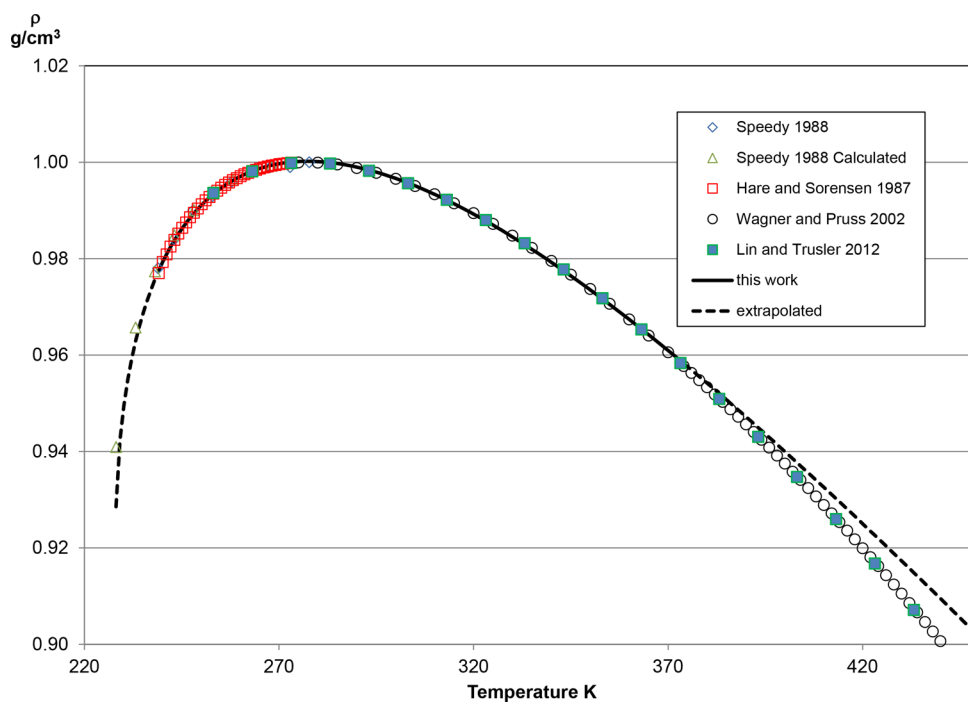
$$\begin{aligned} \Delta C_p^\circ(\text{J/Kmol}) = & -19656.303 + 98.468097(T/\text{K}) \\ & + 2.3432088 \cdot 10^{-8} \cdot (T/\text{K})^{-2} \\ & - 0.1386227 \cdot (T^2) \end{aligned} \quad (32)$$

The fitted  $\Delta C_p^\circ$  compared with the equation by Thurmond and Brass<sup>7</sup> is presented in Figure 3.

**$\Delta G^\circ$  and  $K$  for the reaction  $\text{H}_2\text{O}(\text{ice}) = \text{H}_2\text{O}(\text{l})$ .** The value of 6009.5 J/mol is used for heat of fusion of ice at reference temperature 273.15 K.<sup>31</sup>

From eqs 12 and 32 we can evaluate for heat of fusion of ice as a function of temperature:

$$\begin{aligned} \Delta H^\circ(\text{J/mol}) = & 3501286.79 - 19656.303(T/\text{K}) \\ & + 49.2340485(T/\text{K})^2 - 234320890(T/\text{K})^{-2} \\ & - 0.046207566(T/\text{K})^3 \end{aligned} \quad (33)$$



**Figure 4.** Assessed density  $\rho$  of liquid water compared with experimental data.<sup>15,23,33,34</sup> Dotted lines indicate extrapolated values. Data by Speedy<sup>15</sup> and Lind and Trusler<sup>34</sup> were not included in the assessment.

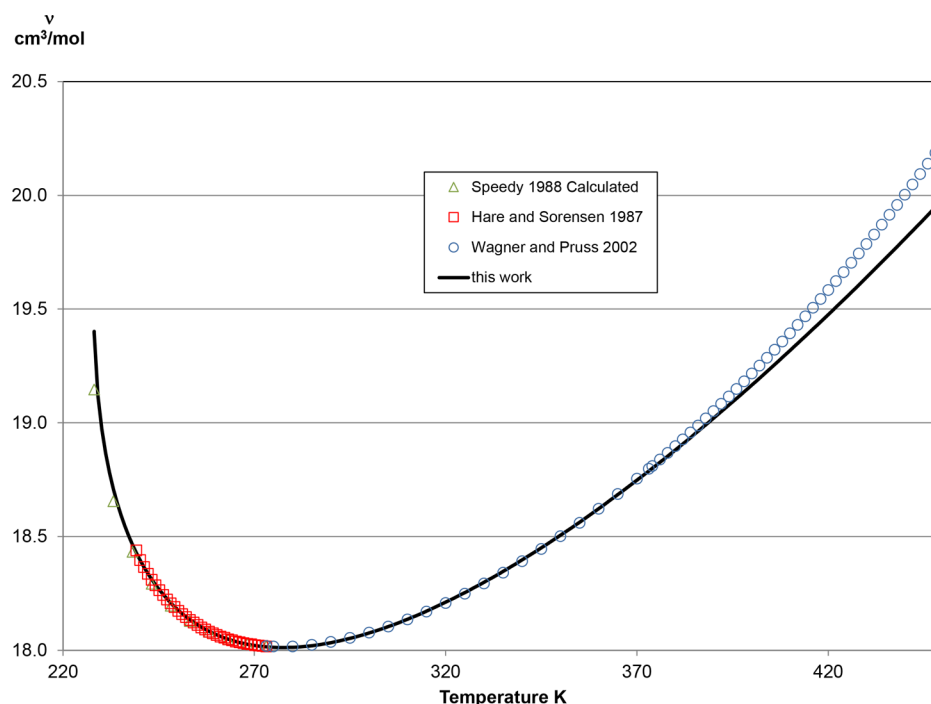


Figure 5. Calculated molar volume  $\nu$  of liquid water compared with literature data.<sup>15,23,33</sup>

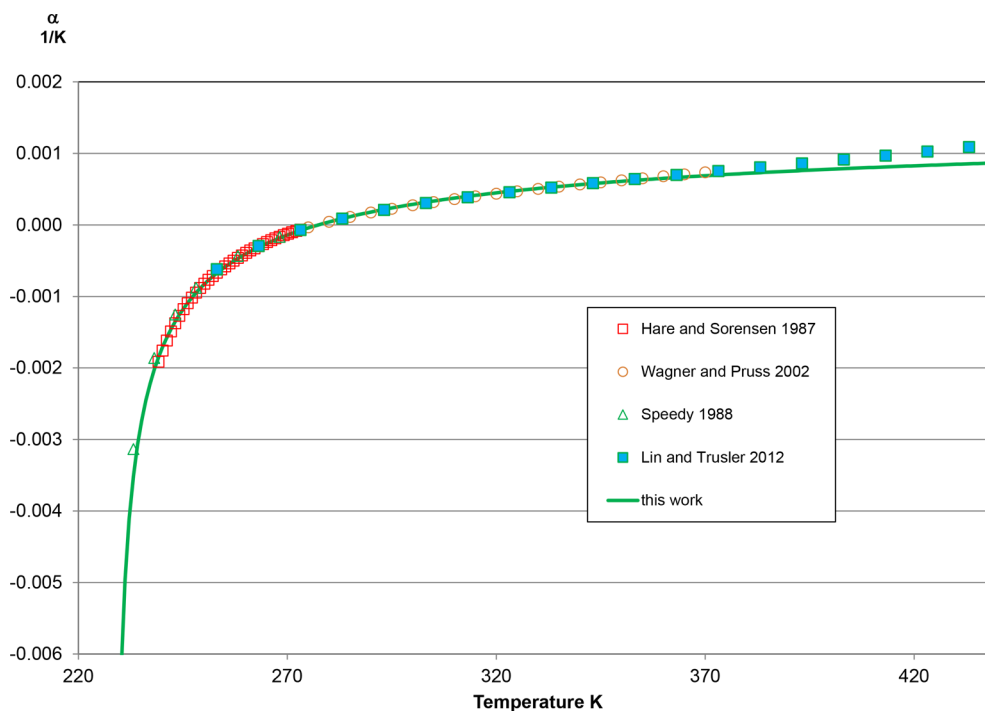


Figure 6. Calculated thermal expansion coefficient of liquid water compared with the literature values.<sup>15,23,33,34</sup>

Thus, the following equations will be obtained from eqs 11–13, and 32:

$$\Delta G^\circ = 3501286.89 - 109795.687T + 19656.303T \ln(T) - 49.2340485T^2 + 0.023103783T^3 - 117160445/T \quad (34)$$

$$\ln(K) = -421105.608/T + 13205.3106 - 2364.09638 \ln(T) + 5.92146122T - 0.0027787306T^2 + 14091079/T^2 \quad (35)$$

A comparison between the equilibrium constant of this work ( $K$ ) with the equilibrium constant obtained in a thermodynamic modeling of the Na–K–Ca–Mg–Cl–SO<sub>4</sub>–H<sub>2</sub>O system at temperatures below 25 °C according to Spencer et al.<sup>32</sup> in 1990, is displayed in Table 5.

As can be seen from Table 5, the difference in equilibrium constant values is less than  $-0.0006$ .

**Volumetric Properties. Liquid Water.** The density for supercooled water was assessed from the recent data of Hare and Sorensen,<sup>33</sup> and Wagner and Pruss.<sup>23</sup> Instead of a sixth degree

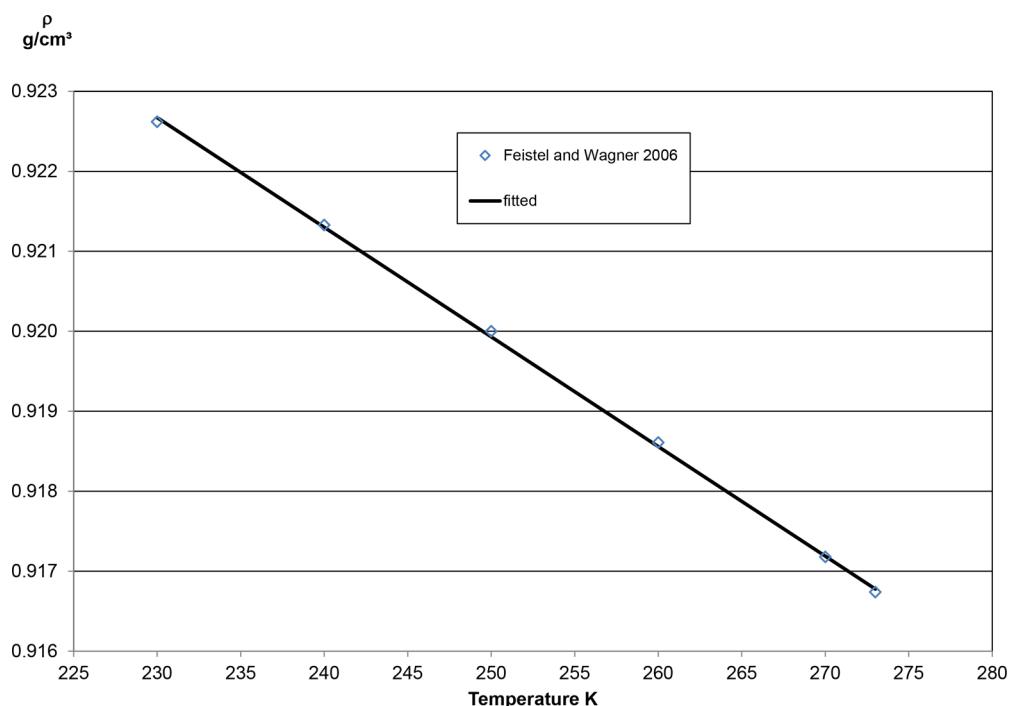


Figure 7. Assessed density  $\rho$  of solid ice compared with the model of Feistel and Wagner.<sup>28</sup>

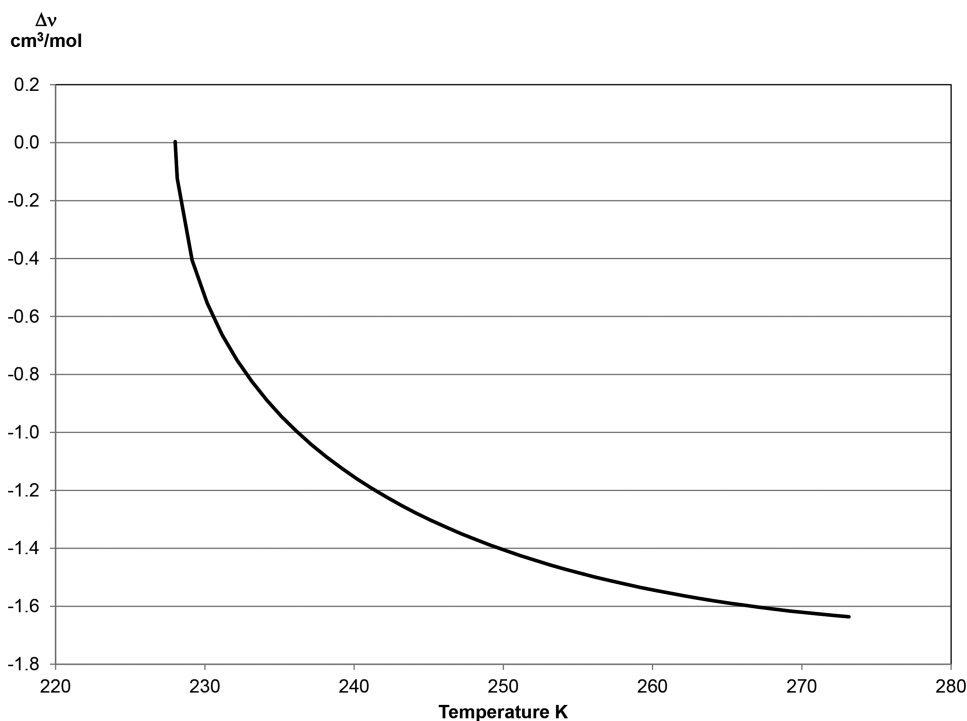


Figure 8. Calculated molar volume difference  $\Delta\nu = \nu_w - \nu_{ice}$  between supercooled water and solid ice.

polynomial equation used by Hare and Sorensen,<sup>33</sup> a similar equation by Speedy<sup>15</sup> with one additional parameter  $A$  was used so that density could be fitted in the entire temperature range  $-34$  to  $+100$  °C.

Thus, the equations for density  $\rho$ , molar volume  $\nu$ , and thermal expansion coefficient  $\alpha$  of water are

$$\rho = \rho_o \exp\{-T_c(A + B\varepsilon + 2C\varepsilon^{1/2})\} \quad (36)$$

$$\nu = \frac{M_{H_2O}}{\rho} = \frac{M_{H_2O}}{\rho_o} \exp\{T_c(A + B\varepsilon + 2C\varepsilon^{1/2})\} \quad (37)$$

$$\alpha = -\frac{1}{\rho} \left( \frac{d\rho}{dT} \right)_p = B + C\varepsilon^{-1/2} \quad (38)$$

where  $\rho_o$ ,  $A$ ,  $B$ , and  $C$  are parameters,  $T$  is temperature in Kelvin.  $M_{H_2O}$  is molecular weight of water, and  $\varepsilon$  is defined as  $T/T_c - 1$ . The data used in the assessment are shown in Table 6.



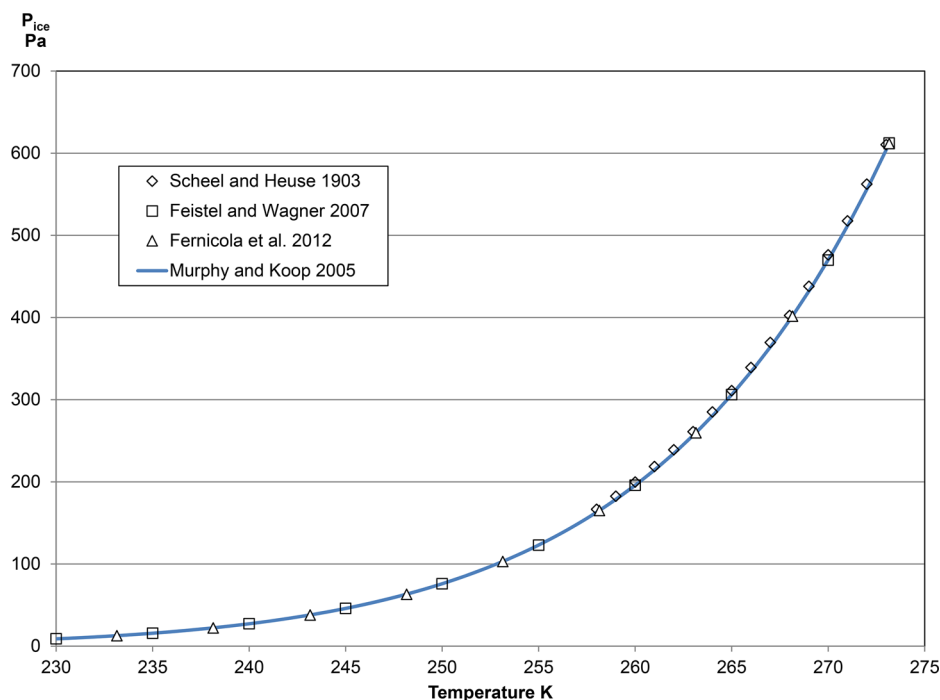


Figure 9. Vapor pressure of ice  $p_{ice}$  according to various authors.<sup>28,36–38</sup>

Table 7. Volume Related Properties of Supercooled Water and Ice at Subzero Temperatures  $T^a$

$T$ (°C)	$T$ (K)	$\nu_w$ (cm <sup>3</sup> /mol)	$\nu_{ice}$ (cm <sup>3</sup> /mol)	$\Delta\nu$ (cm <sup>3</sup> /mol)
0	273.15	18.015	19.651	−1.636
−5	268.15	18.027	19.637	−1.610
−10	263.15	18.049	19.622	−1.573
−15	258.15	18.084	19.607	−1.523
−20	253.15	18.135	19.593	−1.457
−25	248.15	18.208	19.578	−1.370
−30	243.15	18.312	19.563	−1.251
−35	238.15	18.464	19.549	−1.085
−40	233.15	18.710	19.534	−0.824
−45	228.15	19.396	19.520	−0.123

<sup>a</sup> $\nu_w$  is molar volume of liquid water,  $\nu_{ice}$  is molar volume of ice and  $\Delta\nu = \nu_w - \nu_{ice}$ .

Obtained parameters for density for liquid water in the temperature range −34 to 100 °C are

$$\rho_0 = 1.007853(\text{g}/\text{cm}^3), \quad A = 3.9744 \cdot 10^{-04}(1/\text{K}),$$

$$B = 1.6785 \cdot 10^{-03}(1/\text{K}) \quad \text{and}$$

$$C = -7.816510^{-04}(1/\text{K})$$

RMSE and AARD values for Hare and Sorensen's<sup>33</sup> data were 0.0001 g/cm<sup>3</sup> and 0.010%, respectively. For the data by Wagner and Pruss,<sup>23</sup> the corresponding values were 0.0002 g/cm<sup>3</sup> and 0.020%, respectively.

The assessed density of liquid water compared with the experimental data<sup>15,23,33,34</sup> is presented in Figure 4, and the calculated molar volume is in Figure 5.

After completing the density assessment it was noticed that the calculated thermal expansion coefficient are in good agreement up to 100 °C when compared to thermal expansion coefficient data by Hare and Sorensen<sup>33</sup> and Wagner and Pruss.<sup>23</sup> The thermal expansion coefficient from the data by Wagner and

Table 8. Pressure Related Properties at Subzero Temperatures  $T^a$

$T$ (°C)	$T$ (K)	$K$	$p_w$ (Pa)	$p_{ice}$ (Pa)	$\Delta p$ (Pa)	$B$ (cm <sup>3</sup> /mol)
0	273.15	1.000	611.15	611.15	0.00	−1116
−5	268.15	0.953	401.76	421.74	19.98	−1226
−10	263.15	0.907	259.89	286.44	26.55	−1345
−15	258.15	0.864	165.29	191.29	26.00	−1472
−20	253.15	0.823	103.25	125.48	22.23	−1608
−25	248.15	0.784	63.28	80.75	17.46	−1752
−30	243.15	0.747	38.01	50.90	12.89	−1904
−35	238.15	0.712	22.35	31.39	9.04	−2064
−40	233.15	0.680	12.84	18.89	6.05	−2233
−45	228.15	0.651	7.21	11.07	3.87	−2410

<sup>a</sup>Notation:  $K$ , equilibrium constant;  $p_w$ , vapour pressure of supercooled water;  $p_{ice}$ , vapour pressure of ice.  $\Delta p = p_w - p_{ice}$  and  $B$  is the second virial coefficient of water vapour. Vapour pressure of supercooled water is calculated using equation 25.

Pruss<sup>23</sup> was calculated using eq 38 in which the partial derivative of density at standard pressure was calculated by FluidCal.<sup>35</sup>

As can be seen from Figures 4–6, the assessed density and thermal expansion coefficient derived from it, agree well with the literature data and the obtained equations have good extrapolation capabilities especially to lower temperatures.

**Ice Ih.** The density of ice was fitted from the data of Feistel and Wagner<sup>28</sup> in the temperature range (230–273.15) K. A linear fit was found satisfactory as can be seen in Figure 7, with linear correlation coefficient 0.9998 obtained. Thus, the following equations are obtained for ice:

$$\rho_{ice} = A + BT \quad (39)$$

$$\nu_{ice} = \frac{M_{H_2O}}{\rho_{ice}} = \frac{M_{H_2O}}{A + BT} \quad (40)$$

where  $A = 0.954205$  and  $B = -0.0001371$  (K<sup>−1</sup>).



**Table 9.** Values of  $Q$  Parameters and Correlated Pressure ( $p_w$ ) of Supercooled Water Calculated by Equation 23<sup>a</sup>

$T$ (°C)	$T$ (K)	$Q_1$	$Q_2$	$Q_3$	$p_{w,corr}$ (Pa)	$\Delta p$ (Pa)
0	273.15	1.0001	1.0000	1.0000	611.20	0.04
−5	268.15	1.0001	1.0000	1.0000	421.71	0.04
−10	263.15	1.0001	1.0000	1.0000	286.38	0.03
−15	258.15	1.0001	1.0000	1.0000	191.23	0.02
−20	253.15	1.0001	1.0000	1.0000	125.42	0.01
−25	248.15	1.0001	1.0000	1.0000	80.70	0.01
−30	243.15	1.0001	1.0000	1.0000	50.86	0.00
−35	238.15	1.0001	1.0000	1.0000	31.36	0.00
−40	233.15	1.0000	1.0000	1.0000	18.87	0.00
−45	228.15	1.0000	1.0000	1.0000	11.06	0.00

<sup>a</sup>Vapour pressure of supercooled water in calculation of  $Q_2$  and  $Q_3$  parameters is obtained by using equation 25.

**Volume Difference between Supercooled Water and Solid Ice.** Molar volume difference between supercooled water and solid ice can now be calculated from equation  $\Delta v = v_w - v_{ice}$ . Obtained values are shown in Figure 8. It is interesting to find out that the volume difference disappears when temperature approaches the critical temperature 228 K.

## VAPOR PRESSURE

Murphy and Koop<sup>36</sup> have derived the following equation for the vapor pressure of ice when temperature is over 110 K:

$$\ln(p_{ice}^*/Pa) = b_0 + b_1/T + b_2 \ln(T/K) + b_3 T \quad (41)$$

where  $b_0 = 9.550426$ ,  $b_1 = -5723.265$  K,  $b_2 = 3.53068$ , and  $b_3 = -0.00728332$  K<sup>−1</sup>. Analytical eq 41 with a comparison with the literature data is presented in Figure 9.

As can be seen, the equation for the fitted vapor pressure of ice by Murphy and Koop<sup>36</sup> is in good agreement with the

literature data. Assuming all  $Q_i$ 's are equal to 1 in eq 23 we end up with eq 25 as

$$p_w^* \approx p_{ice}^*/K \quad (25)$$

To test the validity of eq 25, the second virial coefficient at subzero temperatures is needed. No experimental data is available at subzero temperatures; so the second virial coefficient  $B$  was extrapolated from the values by Wagner and Pruss<sup>23</sup> in the temperature range 273.15–323.15 K. The obtained equation with the correlation coefficient value of 0.997 is

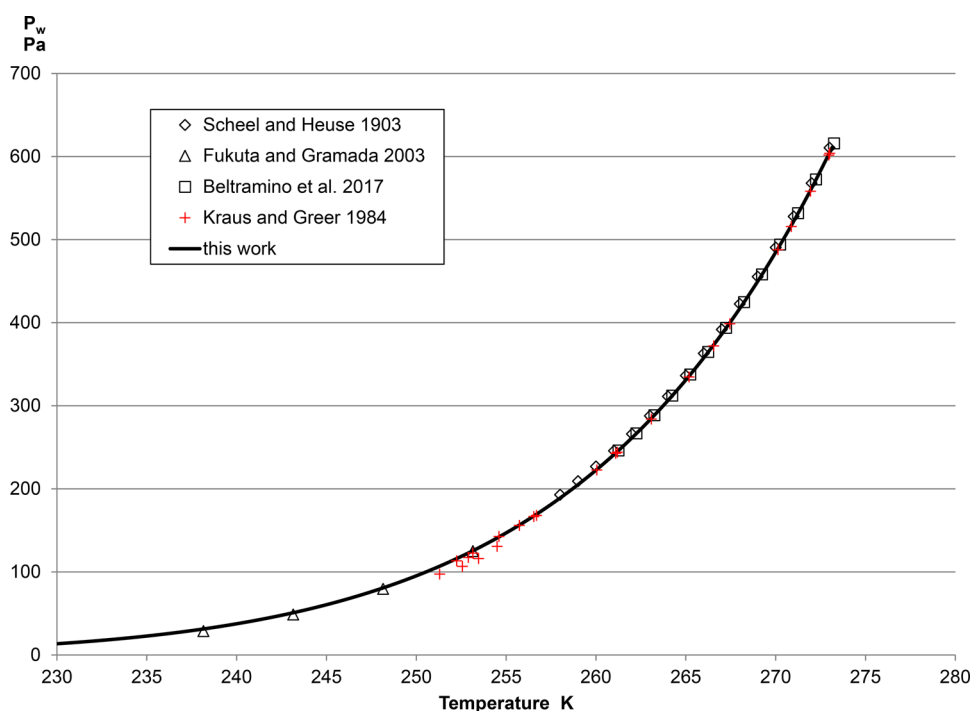
$$B(\text{cm}^3/\text{mol}) = -19362.33 + 112.334 \cdot (T/K) - 0.1667 \cdot (T/K)^2 \quad (42)$$

Volume related properties of supercooled water and ice in the temperature range −45–0 °C are listed in Table 7, pressure related properties in Table 8, and  $Q$  parameters with corrected vapor pressure of supercooled water in Table 9.

As can be seen in Table 9, the pressure correction does not exceed 0.04 Pa and so eq 25 is an excellent approximation for modeling purposes for aqueous solutions at subzero temperatures.

The calculated vapor pressure of pure supercooled water with the literature data is shown in Figure 10 and the pressure difference between pure supercooled water and ice in Figure 11. The calculated vapor pressure of pure supercooled water compared to the values obtained with the equation by Murphy and Koop<sup>36</sup> is presented in Figure 12. The difference with the equation by Murphy and Koop is less than 0.07 Pa using eq 25 and 0.03 Pa using eq 23.

**Activity of Supercooled Water on Ice Curve.** The calculated water activity along the ice-curve is presented in Table 10 and compared with the literature data in Figure 13.



**Figure 10.** Calculated vapor pressure of pure supercooled water  $p_w$  compared with selected literature data.<sup>37,39–41</sup> Not all data by Kraus and Greer<sup>41</sup> is shown on the graph.

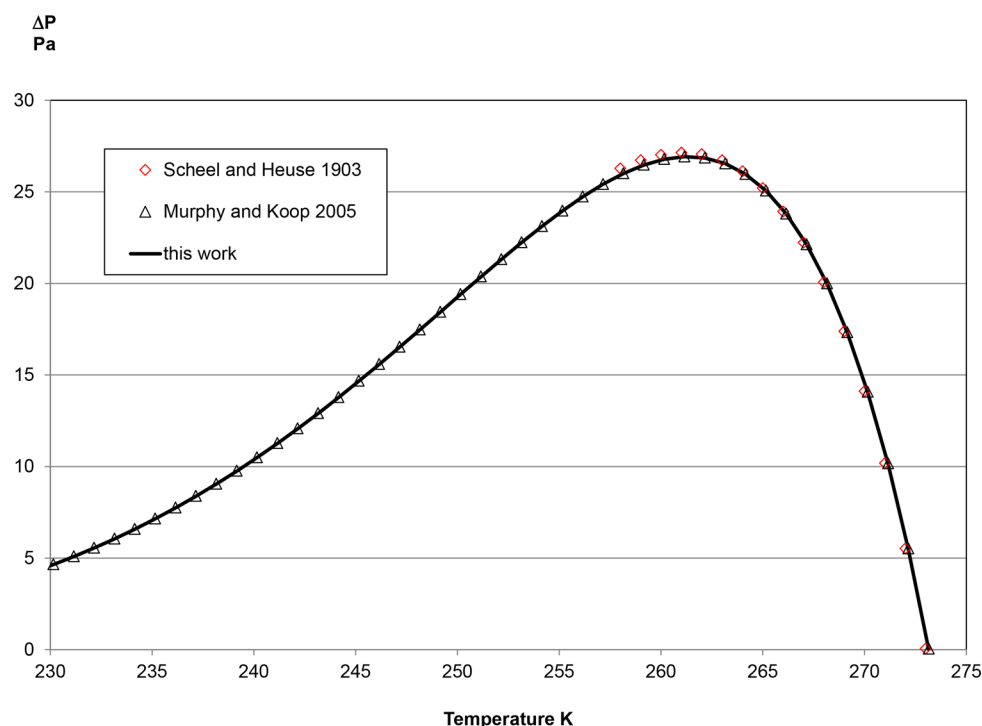


Figure 11. Calculated vapor pressure difference  $\Delta p = p_w - p_{ice}$  between pure supercooled water and ice compared with the literature data.<sup>36,37</sup>

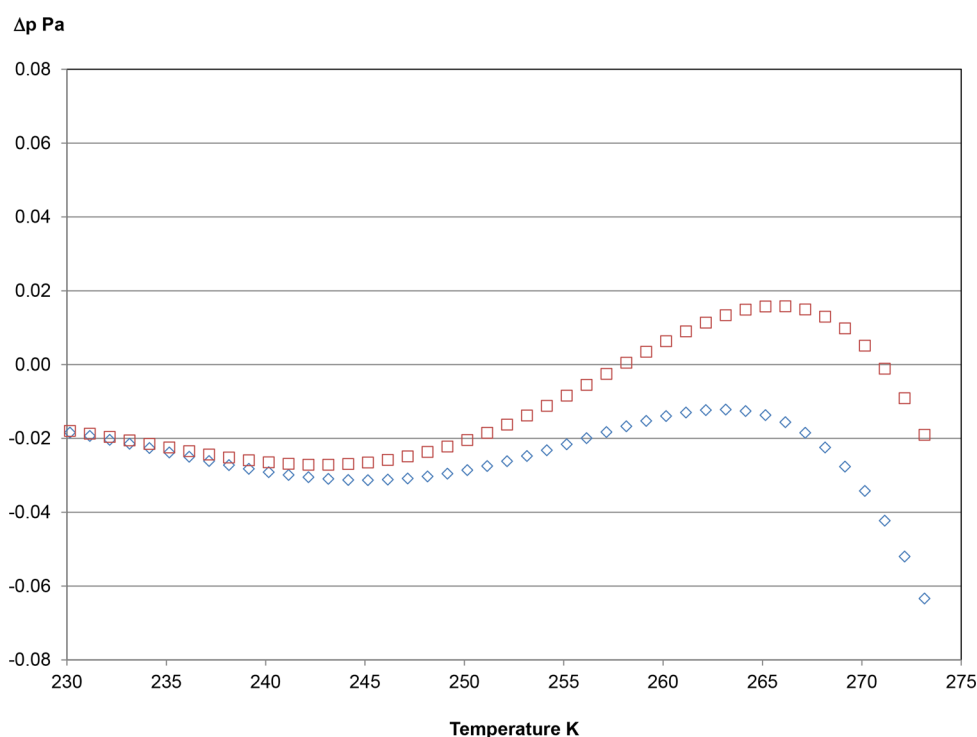


Figure 12. Difference in calculated vapor pressure of pure supercooled water,  $\Delta p = p_{\text{thiswork}} - p_{\text{Koop}}$ , compared with the equation presented by Murphy and Koop.<sup>36</sup> The diamonds (blue) were calculated with eq 25 and squares (red) with eq 23.

As can be seen from Figure 13, the activity of water on ice curve is predicted within  $\pm 0.001$  down to 237 K if values by Murphy and Koop are neglected.

## DISCUSSION AND CONCLUSIONS

A simple model for thermodynamic properties of water from subzero temperatures up to 373 K was derived at ambient

pressure. The heat capacity of supercooled water was assessed as lambda transition. The obtained properties for supercooled water such as heat capacity, vapor pressure, density, and thermal expansion are in excellent agreement with literature data.

Thermodynamic description for the ice-curve in electrolyte solutions is generally obtained in modeling the solubility of ice in the studied electrolyte solution. Thus, the thermodynamic

Table 10. Assessed Activity of Supercooled Water at Ice Curve in 1 atm

T (K)	$a_w$	T (K)	$a_w$	T (K)	$a_w$	T (K)	$a_w$
273.15	1.0000	263.15	0.9073	253.15	0.8229	243.15	0.7467
272.15	0.9904	262.15	0.8985	252.15	0.8149	242.15	0.7396
271.15	0.9808	261.15	0.8898	251.15	0.8070	241.15	0.7326
270.15	0.9713	260.15	0.8811	250.15	0.7991	240.15	0.7256
269.15	0.9619	259.15	0.8726	249.15	0.7914	239.15	0.7188
268.15	0.9526	258.15	0.8641	248.15	0.7837	238.15	0.7121
267.15	0.9434	257.15	0.8557	247.15	0.7762	237.15	0.7054
266.15	0.9342	256.15	0.8473	246.15	0.7687	236.15	0.6989
265.15	0.9252	255.15	0.8391	245.15	0.7613	235.15	0.6925
264.15	0.9162	254.15	0.8309	244.15	0.7540	234.15	0.6862

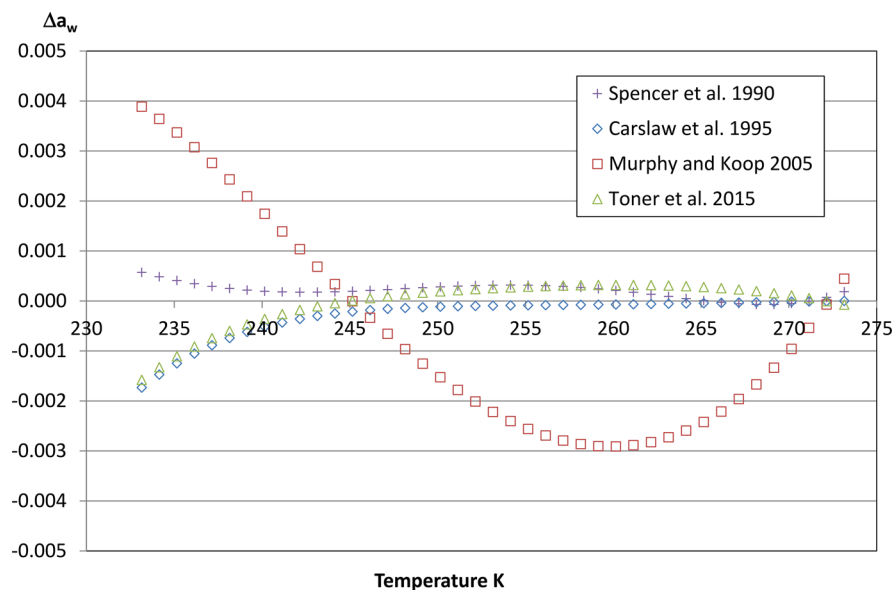


Figure 13. Calculated activity of supercooled water on ice curve compared to activity using eq 10 to equilibrium constants by Murphy and Koop<sup>36</sup> and Spencer et al.<sup>32</sup> as well as polynomial equation with six terms by Carslaw et al.<sup>42</sup> and Toner et al.<sup>1</sup>

Table 11. Values of Debye Hückel Constants. An Outlying Value Obtained by Extrapolating the Equation Adopted by Møller et al.<sup>43</sup> at  $-10^{\circ}\text{C}$  Is Underlined

$t^{\circ}\text{C}$	MTDATA <sup>44</sup>	FactSage <sup>45</sup>	Møller et al. 1988 <sup>43</sup>	Archer and Wang 1990 <sup>46</sup>	Spencer et al. 1990 <sup>32</sup>
-30	0.3639	0.3640	0.3636	0.3535	0.3687
-25	0.3657	0.3658	0.3653	0.3599	0.3698
-20	0.3677	0.3678	0.3671	0.3644	0.3711
-15	0.3697	0.3698	0.3689	0.3679	0.3725
-10	0.3719	0.3720	<u>0.3867</u>	0.3709	0.3742
-5	0.3742	0.3743	0.3744	0.3737	0.376
0	0.3767	0.3768	0.3767	0.3764	0.3781
5	0.3793	0.3795	0.3793	0.3792	0.3804

properties of the ice curve are dependent on the studied electrolyte systems and their number, the excess model used for nonideal behavior of aqueous solution, and the Debye–Hückel constant used.

The values of the Debye–Hückel (DH) equation used varies significantly at subzero temperatures from each other, as can be seen in Table 11. Sometimes the terms used in the DH equation such as  $1/(T - 263\text{ K})$  and  $1/(628\text{ K} - T)$  produce ambiguous values, as noted by Spencer et al.<sup>32</sup>

As can be seen from Table 11, there is a variation between the different DH equations and it increases at lower temperatures. Variation can be expected to increase when first and second derivatives are calculated. Thus, modeled heat capacity of pure supercooled water will depend on the DH equation used if it is obtained by thermodynamic modeling of the apparent heat capacity data.

We suggest a converse procedure. Our equations for heat capacity of supercooled water eqs 26–28 and heat capacity change eq 32 as well as activity of water on ice curve (see Table 10) should be used as the basis for thermodynamic modeling at subzero temperatures. So, the activity of water on the ice curve will form a uniform basis for all electrolyte solutions.

Table 12. Heat Capacity of Supercooled and Ordinary Water up to 373.15 K ( $100^{\circ}\text{C}$ ) in 1 atm Pressure.  $C_p^{\circ}(\text{J/Kmol}) = A + BT + CT^{-2} + D/T^2$

range	temp range (K)	$A_i$	$B_i (\text{K}^{-1})$	$C_i (\text{K}^{-2})$	$D_i (\text{K}^2)$
1	237–262.15	-19654.2	98.5986	-0.138623	$2.343209 \times 10^8$
2	262.15–298.15	134.4	-0.385856	$6.29422 \times 10^{-4}$	
3	298.15–373.15	89.8098	-0.09426775	$1.53047 \times 10^{-4}$	

Several substances form hydrates at subzero temperatures so the activity of water will be included in the solubility product of the precipitated hydrate. Thus, the solubility is connected with the thermodynamic properties of ice and supercooled water via the used activity coefficient model. If the heat capacity of precipitated hydrate is measured from subzero temperature up to 298.15 K, a link between the critically evaluated thermodynamic data and thermodynamic properties of water is formed which enables a critical evaluation of thermodynamic properties of the hydrate.

Generally, heat capacity in thermodynamic and engineering software are expressed as a polynomial equation. Combining heat capacity data of ice and heat capacity change data between ice and supercooled water, these parameters for polynomial equations are obtained (Table 12).

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